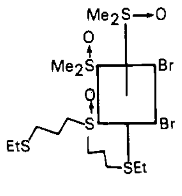
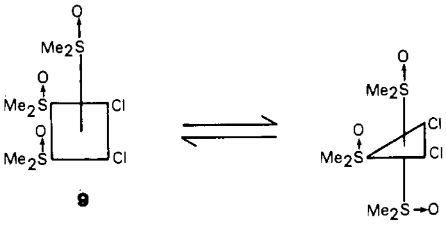
structure **8**. Loss of the dimethyl sulfoxide trans to the thioether



8

ligand of **8** followed by coordination of the remaining thioether atom of ligand **3** would produce the observed product.

For cis-chloro complex **5**, displacement of the more weakly bound axial O-bound sulfoxide of the *cis*-$RuCl_2(Me_2SO)_4$ complex should occur first[10] to form a square-pyramidal intermediate complex, **9**.



9

10

Such an intermediate is actually the initial intermediate along the reaction coordinate of the Berry interconversion that yields **6**. Interconversion of **9** would generate the five-coordinate complex **10**, which has the same geometry as complex **6**. The subsequent complexation of ligand **3** should occur via the same pathway as outlined above for the bromo complex. Thus, while the occurrence of the same structure for complexes **4** and **5** is surprising, it can be rationalized as a logical consequence of this substitution model. This observation provides additional support for such an interpretation of the mode of coordination of tridentate ligand **3** to ruthenium(II).

The surprising inertness of complexes **4** and **5** toward oxygen oxidation can be understood by examining the oxidation potential of each complex. In methylene chloride solution, both **4** and **5** exhibit one irreversible one-electron oxidation by cyclic voltammetry, at 1.45 and 1.42 V, respectively. Such high oxidation potentials reveal that these complexes are very difficult to oxidize. Thus, such structures would be poor candidates for the oxygen-active species formed in these catalytic systems. Further, the high oxidation potential of these complexes also points to enhanced stability of the highest occupied molecular orbital (HOMO) of this isomer relative to that of the other isomers of this stoichiometry.[3] It is also interesting to note that the geometry of these complexes is different from those previously observed with other ligands, and we find that complexes **4** and **5** each oxidize at a potential very different from those observed with other isomers.[3b]

The problem of synthesizing an all-trans complex is clearly more complex than one might imagine. It appears that controlling the stereochemistry of such isomeric complexes is difficult due to the interconversion of five-coordinate intermediates via a pseudorotation process.

Acknowledgment. We wish to thank L. C. Strickland (of these laboratories) for his assistance with the X-ray structure determination of complex **5**, R. E. Shumate for his assistance with the syntheses and separations, and Professor Devon Meek of The Ohio State University for discussions of this work.

Registry No. **1**, 101810-60-0; **2**, 101810-61-1; **3**, 101810-62-2; **4**, 101834-82-6; **5**, 101834-83-7; NaSEt, 811-51-8; *trans*-$RuBr_3(Me_2SO)_4$, 72904-46-2; *cis*-$RuCl_2(Me_2SO)_4$, 59091-96-2; 3,3′-thiodipropanol, 10595-09-2.

Supplementary Material Available: Listings of crystal data, data collection details, and atomic coordinates for **4** and anisotropic thermal parameters, H atom coordinates, bond lengths, bond angles, and torsion angles for the chelate rings for both **4** and **5** (11 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (25 pages), are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Ruthenium(II)-Catalyzed Thioether Oxidation. 3. Syntheses and Structure of Model Complexes with the New Linear Tridentate Ligand Bis(3-(ethylsulfinyl)propyl) Sulfide

Dennis P. Riley[1] and Joel D. Oliver*

Received November 1, 1984

A new tridentate mixed-sulfur-donor ligand, bis(3-(ethylsulfinyl)propyl) sulfide (BEPS) (**3**), has been synthesized, and its reaction with *trans*-$RuBr_2(\overline{S(CH_2)_3CH_2})_4$ has been carried out in an attempt to synthesize an *all-trans*-$RuBr_2$(thioether)$_2$(sulfoxide)$_2$ complex. Under a variety of conditions only the same two isomers are obtained: *mer*-(BEPS)-*cis*-Br_2(THT)Ru (**9**) and *fac*-(BEPS)-*cis*-Br_2(THT)Ru (**10**; the major isomer) (THT = tetrahydrothiophene). ^{13}C and ^1H NMR studies indicate **9** to be highly symmetrical by contrast with **10**. The ^{13}C NMR spectrum of the major isomer, **10**, exhibited 11 resonances, which is only consistent with an all-cis, folded structure. The ^{13}C NMR spectrum of the minor isomer, **9**, exhibited seven resonances, which is consistent with several other symmetrical isomers. A single-crystal structure determination of **9** reveals this complex to possess a six-coordinate pseudooctahedral structure consisting of trans-sulfoxide donors, cis-bromo donors, and cis-thioether donors. The complex has pseudomirror symmetry through the Ru(II) ion, the bromo donors, and the thioether donors. The tridentate ligand coordinates meridionally to the Ru(II) ion with six-atom chelate rings in distorted chair conformations. Selected geometrical details are Ru–Br(1) = 2.564 (1) Å, Ru–Br(2) = 2.574 (1) Å, Ru–S(1) = 2.321 (1) Å, Ru–S(2) = 2.340 (1) Å, Ru–S(3) = 2.355 (1) Å, Ru–S(4) = 2.351 (1) Å, and Br–Ru–Br = 93.3 (1)°. The crystals are monoclinic, $P2_1/n$ (nonstandard setting of No. 14), with $a = 10.742$ (1) Å, $b = 12.890$ (2) Å, $c = 15.771$ (2) Å, $\beta = 101.41$ (1)°, and $Z = 4$. Least-squares refinement of the structure on the basis of 2867 unique reflections with $|F| > 4\sigma(|F|)$ has produced $R = 0.034$ and $R_w = 0.038$.

Introduction

In the first paper of this series we reported that an all-trans Ru(II) complex with the stoichiometry $RuX_2(SR_2)_2(R_2SO)_2$ (**1**)[2] is the probable structure for the most oxygen-active species leading to catalysis in these thioether oxidation systems.[3,4]

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(2) Part 1: Riley, D. P.; Oliver, J. D. *Inorg. Chem.*, first of two preceding papers in this issue.

(3) Riley, D. P.; Shumate, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 3179.

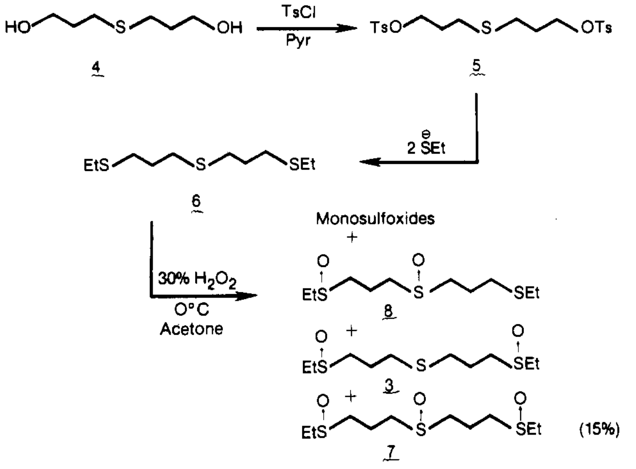

Figure 1. Preparation of the linear tridentate mixed thioether–sulfoxide ligands.

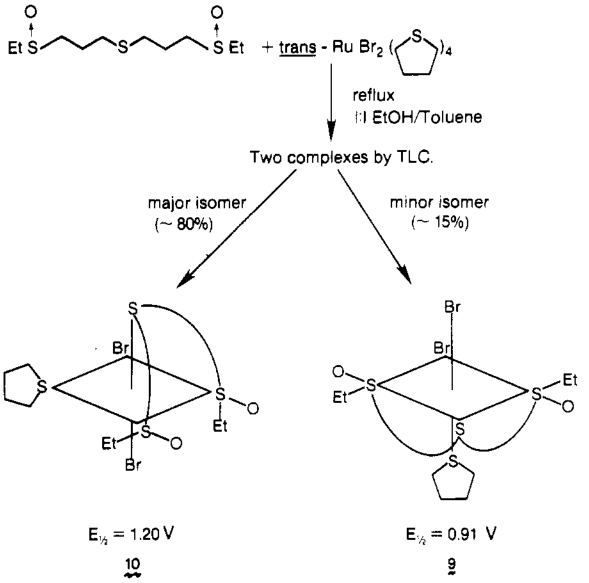

Figure 2. Preparation of the two isomeric complexes, **9** and **10**, $RuBr_2(EtSO(CH_2)_3S(CH_2)_3SOEt)(S(CH_2)_4)$.

In the second paper of this series we described our attempts to synthesis an *all-trans*-$RuX_2(R_2S)_2(R_2SO)_2$ complex from a symmetrical tridentate monosulfoxide ligand, 3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane (EESP). These attempts failed due to isomerization (possibly through a five-coordinate intermediate) to yield cis-halo complexes. In this paper we report the synthesis of a new symmetrical linear tridentate bis(sulfoxide) ligand (Figure 1) containing the sulfoxide–sulfide–sulfoxide donor set. The synthesis and characterization of two isomeric Ru(II) complexes with this ligand are described (Figure 2). In order to structurally characterize these complexes, the crystal structure of minor product **9** of the reaction of *trans*-$RuBr_2(\overline{S(CH_2)_3CH_2})_4$ (**2**) with the ligand bis(3-(ethylsulfinyl)propyl) sulfide (**3**; BEPS) (Figure 2) was determined.

Experimental Section

General Procedures. The majority of the experimental procedures have been described in the first paper in this series. Preparative high-pressure liquid-chromatographic separations were performed on a Waters Prep 500 HPLC system by using a Waters silica-gel stationary-phase column. Vapor pressure osmometry studies were carried out in chloroform solutions on a Knauer vapor pressure osmometer.

Crystallographic Investigation of 9. The crystal data and the details of data collection are given in Table I, and the final atomic coordinates are listed in Table II. The locations of the Ru and Br ions were obtained by using the automatic Patterson solution process of the SHELXTL program.[5] The remaining non-hydrogen atoms were located in a subsequent electron density map. After convergence of the least-squares refinement of the structure with anisotropic thermal parameters, reasonable positions for the majority of the H atoms were revealed in a difference electron density map. The methylene H atoms of the tridentate ligand were easily located. These H atoms were included in the structural model and were refined in subsequent least-squares cycles. The methyl H atoms and the methylene H atoms of the tetrahydrothiophene ligand could not be located precisely due to apparent high thermal motion. These H atoms were included in the structural model at their fixed idealized locations (d(C–H) = 0.96 Å) with isotropic thermal parameters fixed at 1.2 times

Table I. Summary of Crystal Data and Details of Data Collection

Crystal Data			
formula	$C_{14}H_{30}O_2S_4Br_2Ru$	space group	$P2_1/n$
fw	619.5	syst absences	$h0l$ for $h + l$ odd $0k0$ for k odd
a, Å	10.742 (1)[a]	d(calcd), g cm^{-3}	1.92
b, Å	12.890 (2)	F(000)	1232
c, Å	15.771 (2)	T, °C	21
β, deg	101.41 (1)	Z	4
vol, Å^3	2140.6		

Data Collection	
cryst dimens, mm	0.10 × 0.12 × 0.32
λ(Mo K$\bar{\alpha}$), Å	0.71073
μ(Mo K$\bar{\alpha}$), cm^{-1}	48.0
limiting sphere, deg	$2.5 < 2\theta < 50.0$
scan mode	θ–2θ
scan rate, deg/min	variable, 4–29.3
Miller indexes collcd	$(h,k,\pm l)$
no. of reflcns measd	4205
no. of unique reflcns measd	3983
no. of reflcns used ($F_o > 4\sigma(F_o)$)	2867
merging R	0.013
check reflcns[b]	(002, 060, 400, 336)
abs cor	empirical as a fctn of ψ
min/max trans factors	0.21/0.27

[a] Lattice constants were obtained from a least-squares refinement of the setting angles of 25 general reflections. [b] Analysis of these intensities revealed only random variations (<2% relative) from their mean intensities.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for Non-Hydrogen Atoms of **9**

atom	x	y	z	U[a]
Ru	2482 (1)	7260 (1)	5401 (1)	27 (1)
Br(1)	4845 (1)	7099 (1)	5349 (1)	46 (1)
Br(2)	2012 (1)	8459 (1)	4072 (1)	46 (1)
S(1)	2994 (1)	8701 (1)	6284 (1)	36 (1)
S(2)	2710 (1)	6155 (1)	6599 (1)	34 (1)
S(3)	2025 (1)	5878 (1)	4411 (1)	31 (1)
S(4)	295 (1)	7315 (1)	5402 (1)	37 (1)
O(1)	1949 (4)	9227 (3)	6589 (2)	50 (1)
O(2)	680 (3)	5604 (3)	4086 (2)	41 (1)
C(1)	4055 (7)	10687 (4)	6293 (4)	66 (3)
C(2)	3839 (7)	9679 (5)	5799 (4)	55 (2)
C(3)	4192 (5)	8446 (4)	7241 (3)	48 (2)
C(4)	3810 (6)	7610 (4)	7804 (3)	48 (2)
C(5)	3981 (6)	6521 (5)	7487 (4)	46 (2)
C(6)	3364 (5)	4901 (4)	6422 (3)	42 (2)
C(7)	2574 (6)	4333 (4)	5664 (4)	44 (2)
C(8)	2817 (5)	4694 (4)	4803 (3)	42 (2)
C(9)	2729 (6)	6058 (4)	3471 (3)	50 (2)
C(10)	2547 (7)	5130 (5)	2866 (4)	66 (3)
C(11)	−459 (5)	8589 (4)	5249 (4)	52 (2)
C(12)	−1376 (10)	8599 (7)	5824 (7)	145 (6)
C(13)	−1201 (7)	7877 (6)	6481 (5)	88 (4)
C(14)	−91 (5)	7167 (5)	6469 (4)	55 (2)

[a] Equivalent isotropic U is defined as $^1/_3$(trace U_{ij}).

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(4) Riley, D. P. Paper presented at the Tenth Organic Reactions Catalysis Society Conference, Williamsburg, PA, May 7–9, 1984.

(5) Sheldrick, G. M. *SHELXTL: An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Nicolet: Madison, WI, 1984.

the equivalent isotropic thermal parameter of the parent atom. The parameters that were refined in the final least-squares cycles were an overall scale factor, the positional and anisotropic thermal parameters of the non-hydrogen atoms, and positional and isotropic thermal parameters of the methylene H atoms of ligand **3**. The weighting function was computed according to $w = (\sigma^2(|F_o|) + 0.0005|F_o|^2)^{-1}$, where $\sigma(|F_o|)$ is the standard deviation of the structure factor based solely on counting statistics. The final values of R and R_w are 0.034 and 0.038. The goodness-of-fit parameter was 1.1. A final difference electron density map showed a featureless background below 0.5 e Å^{-3}, except for six peaks with magnitudes <0.9 e Å^{-1} within 1 Å of a Ru, Br, or S atom.

All structural calculations were made on a Data General Eclipse computer by using the SHELXTL software package. The scattering factors for all atoms and the real and the imaginary corrections for anomalous dispersion were taken from ref 6.

Syntheses. Bis(3-(ethylsulfinyl)propyl) Sulfide (3). The first step of this synthesis has been described previously[7] and simply involves the conversion of 3,3′-thiodipropanol (**4**) to its ditosylate (**5**) by standard procedures.[8] The ditosylate was then reacted with 2 equiv of NaSEt to afford symmetrical, linear tridentate tris(thioether) ligand **6**. In a typical preparation, 28.2 g (0.118 mol) of **6** were dissolved in 100 mL of acetone, which was then cooled to 0 °C. To this solution was added dropwise over a period of 8 h 26.8 g (0.236 mol) of 30% H_2O_2. After the initial addition of 30% H_2O_2 some unreacted starting material remained, so 30% H_2O_2 (10.0 mL) was added dropwise until all starting material had disappeared by TLC. Platinum black was then added with stirring to destroy any excess peroxide. The solution was filtered through Celite and was taken to dryness on a rotary evaporator with the temperature maintained below 30 °C. The resultant white solid was a mixture containing five components: two monosulfoxides, two disulfoxides, and trisulfoxide ligand **7**. This crude material was vigorously stirred with 50 mL of pentane and 50 mL of H_2O. Since the layers that separated were cloudy, methanol (~2 mL) was added dropwise until the layers clarified. The pentane layer contained the monosulfoxide products, and the H_2O/MeOH layer contained the disulfoxide products and trisulfoxide compound **7**. The H_2O/MeOH solution was taken to dryness on a rotary evaporator and was then redissolved in 50 mL of hot acetone. When this solution was cooled to −40 °C, a white crystalline product formed and was collected by filtration. This material was the trisulfoxide ligand **7**, which was identified by its mass spectrum (parent ion with m/e 286, calcd m/e 286), ^{13}C NMR spectrum, and elemental analysis. The yield of compound **7** was 5.2 g (15%).

The acetone solution containing disulfoxide ligands **3** and **8** was stripped to dryness on a rotary evaporator to yield 16.6 g of the crude mixture of disulfoxides. Five grams of this mixture was dissolved in 5.0 mL of 3.5% MeOH in CH_2Cl_2. This solution was injected into the HPLC instrument and was separated by using 3.5% MeOH in CH_2Cl_2 as the eluent. The fractions were analyzed by analytical reverse-phase HPLC (Waters C18 column, 30 cm × 3.9 mm) by using 1.5% H_2O in CH_3CN as the solvent. The fractions containing the pure disulfoxide ligands, **3** and **8**, were retained, while the mixed fractions were recombined and recycled through preparative HPLC under identical conditions to give additional enriched fractions. From these two fractions, solids were obtained by removing the solvent on a rotary evaporator. Recrystallization (from Et_2O plus a minimum volume of CH_2Cl_2 to give a clear solution) of these solids gave pure **3** and pure **8**. The yield of pure BEPS (**3**) was 1.0 g while the yield of pure **8** was 1.1 g. For both isomers, the mass spectra (parent ion m/e 270, calcd m/e 270) confirmed the stoichiometry. Anal. Calcd for each isomer of $C_{10}H_{22}O_2S_3$: C, 44.41; H, 8.20; S, 35.56; O, 11.83. Found for symmetrical disulfoxide ligand **3**: C, 44.64; H, 8.23; S, 35.63; O, 11.77. ^{13}C NMR spectrum of **3**: δ 49.05, 44.84, 29.76, 21.58, 5.87. ^{13}C spectrum of **8**: δ 50.83, 50.54, 49.56, 45.61, 30.04, 25.37, 22.09, 16.82, 14.37, 6.45.

Two Isomers of Dibromo(tetrahydrothiophene)[bis(3-(ethylsulfinyl)propyl) sulfide]ruthenium(II), $RuBr_2(\overline{S(CH_2)_3CH_2})(EtSO(CH_2)_3S(CH_2)_3SOEt)$ (9 and 10). Under a nitrogen atmosphere, 0.75 g (1.2 mmol) of *trans*-$RuBr_2(\overline{S(CH_3)_2CH_2})_4$[2,3] was stirred in 100 mL of hot ethanol. To this solution was added 0.33 g (1.2 mmol) of symmetrical disulfoxide ligand **3**. The solution was heated to reflux, and toluene (25 mL) was added until the solids dissolved. The solution was stirred for an additional $^1/_2$ h, after which time TLC on silica gel with 95% CH_2Cl_2/5% MeOH as eluent revealed that all the starting material had been consumed and that two closely eluting products (R_f ~0.60 and 0.65) were present. The solvent was removed via a rotary evaporator, and the yellow-orange residue was dissolved under N_2 in a minimum volume of boiling MeOH (~30 mL). This solution was allowed to cool slowly to room temperature and was stored undisturbed for 16 h. Large orange crystals formed and were collected by filtration and dried in vacuo. The yield of this product was 0.11 g (14%)—corresponding to minor isomer **9** (R_f = 0.65). The remaining solution was reduced to 15 mL and was stored at −40 °C for several days, whereupon yellow crystalline clusters formed. The crystalline product was collected by filtration, washed with cold MeOH, and dried in vacuo. The yield of this major isomer, **10** (R_f ~0.60), was 0.33 g (42%).

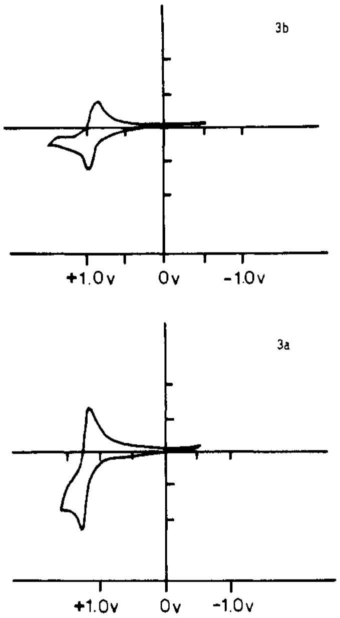

Figure 3. (a) Cyclic voltammogram of a 6.0 × 10^{-3} M solution of **10** in CH_2Cl_2. The scan was initially in the oxidative (positive) direction beginning at 0 V at the rate of 100 mV/s. (b) Cyclic voltammogram of a 3.0 × 10^{-3} M solution of **9** in CH_2Cl_2. The scan was initially in the oxidative direction beginning at 0 V at a rate of 100 mV/s.

When the preparation was repeated with the reaction solvent as pure toluene, CH_2Cl_2, or $CHCl_3$, only one spot was observed by TLC and only one product was obtained—isomer **10**. Anal. Calcd for isomers **9** and **10**, $C_{14}H_{30}Br_2O_2S_4Ru$: C, 27.14; H, 4.88; Br, 25.80; S, 20.70. Found for major isomer **10**: C, 27.27; H, 4.99; Br, 25.71; S, 20.63. ^{13}C NMR spectrum of isomer **9**: δ 5.38, 19.27, 28.24, 34.28, 37.42, 48.44, 49.08. ^{13}C NMR for isomer **10**: δ 5.53, 6.17, 17.94, 18.66, 29.64, 32.14, 35.45, 47.14, 50.14, 50.31, 52.55. Electronic spectrum, λ^{max}, 10^3 cm^{-1} (ε): isomer **9**, 21.7 (118), 26.3 (360), 38.2 (7200); isomer **10**, 24.7 (535), 29.3 (336), 38.2 (6490).

Results

Syntheses and Characterizations. The synthesis of new linear tridentate ligands **3**, **7**, and **8** is shown schematically in Figure 1. It was anticipated that the reaction of **3** with the *trans*-$RuBr_2(\overline{S(CH_2)_3CH_2})_4$[2,3] complex (**2**) would give an isomer with all-trans structure **1**.[2] Instead, this reaction gave either a mixture of two isomers in alcoholic solvents (Figure 2) or in nonhydroxylic solvents one product, major isomer **10**. In addition, attempts to isomerize these two isomers by prolonged heating in refluxing 2-methoxyethanol has no effect on their respective structures.

The solid-state infrared spectrum of complex **9** reveals the presence of one S→O sulfoxide stretch at 1078 cm^{-1}, indicating a structure with equivalent terminal sulfoxides. In contrast, major isomer **10** possesses two S→O stretching frequencies, at 1070 and 1080 cm^{-1} (e.g., the S→O stretch in the free ligand occurs at 1030 cm^{-1}),[9] suggesting a structure with different environments for the sulfoxide ligands for this isomer. The increase in the S→O

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(6) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(7) Part 2: Riley, D. P.; Oliver, J. D. *Inorg. Chem.*, second of two preceding papers in this issue.

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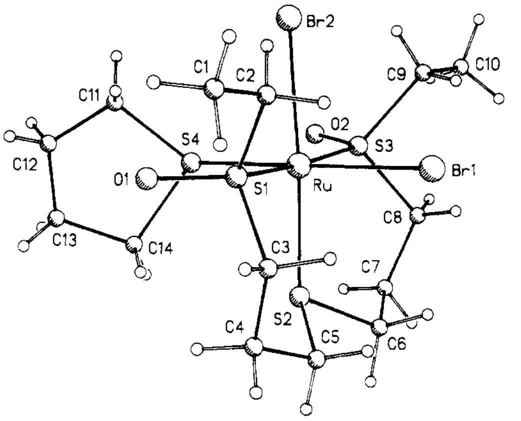

Figure 4. Perspective drawing of complex **9**, *cis*-dibromo(tetrahydrothiophene)[bis(3-(ethylsulfinyl)propyl) sulfide)]ruthenium(II), illustrating the atom-labeling scheme.

stretching frequency for the complexes when compared to the free ligand confirms that these complexes contain S-bound sulfoxide donors.[9] The cyclic voltammogram of each complex (Figure 3) reveals the presence of one pseudoreversible oxidation wave at $E_{1/2} = 1.20$ V for complex **10** and $E_{1/2} = 0.91$ V for complex **9** and confirms the TLC results that these two crystalline materials are each one isomer.

The ^{13}C NMR spectra of these complexes are particularly informative. For minor isomer **9**, there are seven distinct resonances: two resonances for the C atoms adjacent to the sulfoxide at δ 48.4 and 49.1, two resonances due to the lone tetrahydrothiophene ligand at δ 28.2 and 37.4, a single resonance at δ 19.3 for the central methylene of the trimethylene linkages, and a single resonance for the methyl group at δ 5.4. This pattern is consistent with either of the three possible structures (B, D, or E in Figure 1 of ref 2), having a symmetrical environment for the ligands (isomer A is impossible using the chelating tridentate ligand **3**).

The ^{13}C NMR spectrum of the unsymmetrical major isomer shows an 11-line pattern that has four downfield resonances (δ 52.6, 50.3, 50.1, and 47.1) due to the C atoms α to the sulfoxide groups, two resonances due to the bound tetrahydrothiophene ligand at δ 29.6 and 35.5, a doubly intense resonance at δ 32.1 due to the two (apparently equivalent) methylene C atoms α to the thioether S atom, two distinct resonances at δ 17.9 and 18.7 corresponding to the nonequivalent central C atoms of the two trimethylene linkages, and two methyl C resonances at δ 5.5 and 5.2 corresponding to nonequivalent terminal methyl groups of the tridentate ligand. The solution molecular weight of **10** was determined by osmometry and found to be 601 (calcd, 621), confirming a monomeric structure for this complex. Thus, on the basis of this result and the spectral results, it is possible to unambiguously assign the structure of complex **10** to the dissymmetric all-cis folded structure containing an unsymmetrical tridentate ligand environment, corresponding to isomer C of Figure 1 in the first paper in this series.[2]

X-ray Crystal Structure of 9. To identify the structure of minor isomer **9** produced in these reactions, the molecular structure was determined on a crystal obtained from ethanol solution. A perspective drawing of the result of the crystal structure analysis is shown in Figure 4. Bond lengths and bond angles are given in Table III. The structure corresponds to isomer E of Figure 1 in ref 2 and consists of a six-coordinate, pseudooctahedral Ru(II) complex with cis-bromide, cis-thioether, and trans-sulfoxide donor groups. The tridentate sulfoxide–thioether–sulfoxide ligand coordinates meridionally to the Ru(II) ion.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **9**

Ru–Br(1)	2.564 (1)	Ru–Br(2)	2.574 (1)
Ru–S(1)	2.321 (1)	Ru–S(2)	2.340 (1)
Ru–S(3)	2.355 (1)	Ru–S(4)	2.351 (1)
S(1)–O(1)	1.471 (4)	S(1)–C(2)	1.810 (7)
S(1)–C(3)	1.809 (5)	S(2)–C(5)	1.814 (6)
S(2)–C(6)	1.807 (6)	S(3)–O(2)	1.477 (4)
S(3)–C(8)	1.797 (5)	S(3)–C(9)	1.808 (6)
S(4)–C(11)	1.825 (6)	S(4)–C(14)	1.822 (7)
Br(1)–Ru–Br(2)	93.3 (1)	Br(1)–Ru–S(1)	88.0 (1)
Br(2)–Ru–S(1)	89.6 (1)	Br(1)–Ru–S(2)	91.8 (1)
Br(2)–Ru–S(2)	174.8 (1)	S(1)–Ru–S(2)	91.6 (1)
Br(1)–Ru–S(3)	89.7 (1)	Br(2)–Ru–S(3)	86.1 (1)
S(1)–Ru–S(3)	175.1 (1)	S(2)–Ru–S(3)	92.9 (1)
Br(1)–Ru–S(4)	176.6 (1)	Br(2)–Ru–S(4)	87.0 (1)
S(1)–Ru–S(4)	95.4 (1)	S(2)–Ru–S(4)	87.9 (1)
S(3)–Ru–S(4)	86.9 (1)	Ru–S(1)–O(1)	117.4 (2)
Ru–S(1)–C(2)	112.5 (2)	O(1)–S(1)–C(2)	107.2 (3)
Ru–S(1)–C(3)	113.6 (2)	O(1)–S(1)–C(3)	105.9 (2)
C(2)–S(1)–C(3)	98.4 (3)	Ru–S(2)–C(5)	114.0 (2)
Ru–S(2)–C(6)	113.7 (2)	C(5)–S(2)–C(6)	95.5 (3)
Ru–S(3)–O(2)	118.2 (2)	Ru–S(3)–C(8)	113.1 (2)
O(2)–S(3)–C(8)	106.3 (2)	Ru–S(3)–C(9)	112.4 (2)
O(2)–S(3)–C(9)	106.6 (2)	C(8)–S(3)–C(9)	98.3 (3)
Ru–S(4)–C(11)	116.4 (2)	Ru–S(4)–C(14)	114.0 (2)
C(11)–S(4)–C(14)	92.3 (3)		

Table IV. Six-Atom Chelate Ring Torsion Angles (deg) for **9**

i–j–k–l	ω	i–j–k–l	ω
S(2)–Ru–S(1)–C(3)	36.3 (2)	S(2)–Ru–S(3)–C(8)	−31.8 (2)
Ru–S(1)–C(3)–C(4)	−58.9 (5)	Ru–S(3)–C(8)–C(7)	55.2 (4)
S(1)–C(3)–C(4)–C(5)	79.6 (6)	S(3)–C(8)–C(7)–C(6)	−79.7 (5)
C(3)–C(4)–C(5)–S(2)	−78.5 (6)	C(8)–C(7)–C(6)–S(2)	80.2 (6)
C(4)–C(5)–S(2)–Ru	57.9 (5)	C(7)–C(6)–S(2)–Ru	−58.0 (5)
C(5)–S(2)–Ru–S(1)	−36.4 (2)	C(6)–S(2)–Ru–S(3)	33.5 (2)

Discussion

The two complexes isolated from the reaction of the symmetrical bis(sulfoxide) tridentate ligand **3** and *trans*-$\mathrm{RuBr_2(\overline{S(CH_2)_3C}H_2)_4}$ (Figure 2) represent two of the five geometrical isomers that are possible in pseudooctahedral geometry with a 2,2,2 stoichiometry with three different ligands (Figure 1 of ref 2). The desired all-trans complex (**1**) does not form with this ligand. Instead, a complex possessing the geometry in which the tridentate ligand BEPS coordinates in a folded all-cis facial array forms either exclusively or as the major isomer. The identity of this major isomer (**10**) could be determined by ^{13}C NMR spectroscopy because only one of the possible structures, the all-cis isomer, contains an unsymmetrical ligand environment. This structure could possess as many as 12 different magnetically unique ^{13}C centers when SR_2 = tetrahydrothiophene and ligand **3** is present. We observed an 11-line spectrum with the C atoms α to the thioether S atom being equivalent. The other four isomers (A, B, D, and E of Figure 1, ref 2) would be expected to yield seven-line ^{13}C spectra due to their symmetrical ligand environments. This structural assignment is also confirmed by the presence of two distinct S→O stretching absorptions in the infrared spectrum of isomer **10**, indicating that the two terminal sulfoxides of ligand **3** are nonequivalent. These points make it possible to unambiguously assign the structure of this major isomer to the monomeric, unsymmetrical all-cis folded structure.

The oxidation potential ($E_{1/2} = 1.20$ V) of this complex in methylene chloride (Figure 3) also supports this structural assignment. We had previously synthesized an all-cis 2,2,2 complex by the reaction of 3,6-dithiaoctane ($\mathrm{EtSCH_2CH_2SEt}$) with *cis*-$\mathrm{RuCl_2(Me_2SO)_4}$.[2] There were two complexes formed in this reaction, the all-cis complex, $\mathrm{RuCl_2(EtSCH_2CH_2SEt)(Me_2SO)_2}$, and the trans($X_2$), cis,cis isomer. The oxidation potential of the *trans*-dihalo complex has $E_{1/2} = 1.05$ V while that of the all-cis isomer has $E_{1/2} = 1.22$ V.[2,4] These values are apparently characteristic for these geometries since the other geometries of 2,2,2 complexes possess their own unique and different oxidation potentials.[2,7,10] Examples of the all-trans geometry (isomer B) have been made from monodentate ligands and have an oxidation potential with $E_{1/2} \sim 0.75$ V.[2,4] An example of the complex with

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(10) Riley, D. P. Paper presented at the 23rd International Conference on Coordination Chemistry, Boulder, CO, Aug 1984.

trans-dithioether cis,cis geometry (isomer D) has $E_{1/2}$ = 1.45 V.[7] Clearly, the oxidation potential is itself a useful diagnostic tool for the geometry of these 2,2,2 complexes, and the oxidation potential observed for **10** corroborates the all-cis folded structure for this isomer.

The crystal structure analysis reveals that the geometry of minor isomer **9** corresponds to that of isomer E of Figure 1 in ref 2. The perspective drawing of the complex in Figure 4 and the list of endocyclic torsion angles reveal that both chelate rings have distorted chair conformations. Except for the atoms of the tetrahydrothiophene ligand, the complex has a pseudomirror plane of symmetry through the atoms Ru, Br(1), Br(2), S(2), and S(4). The out-of-plane distances are given in the supplementary material and support this pseudosymmetry. The four methylene groups of the tetrahydrothiophene ligand define the only portion of the complex that does not obey this pseudosymmetry due to the geometry of the sp^3 orbitals that the S atom uses to form a σ-bond with the Ru(II) ion. In solution, rotation about the Ru–S(4) bond would be expected to be facile and would account for the time-averaged mirror symmetry that results in a seven-line ^{13}C NMR spectrum for **9**. A similar correlation between the solution ^{13}C NMR spectrum and a nonsymmetric crystal structure holds for the related complex, $\mathrm{RuBr_2(Me_2SO)((EtS(CH_2)_3)_2SO)}$.[7] The consistency between the symmetry of the complex in the solid state and the symmetry of the ^{13}C NMR spectrum for these two complexes suggests that the six-atom chelate rings are sufficiently rigid to maintain their conformation in solution.

An observant reviewer pointed out the large thermal parameters for atoms C(12) and C(13) of the tetrahydrothiophene ligand and suggested that we analyze the directions of the ellipsoids to determine if they are consistent with pseudorotation of the five-membered ring. The major axes for the thermal ellipsoids for both C(12) and C(13) are approximately perpendicular to the ring plane and are consistent with a vibrational mode that interconverts the five-membered ring between envelope and half-chair conformers.

The Ru–S–C–C residues of the ethyl substituents have a trans conformation, and the terminal methyl groups are staggered with respect to their adjacent methylene groups. This conformation of the ethyl substituents minimizes their intramolecular steric interactions. The same conformation of the ethyl groups was seen in the structure of $\mathrm{RuBr_2(Me_2SO)((EtS(CH_2)_3)_2SO)}$.[7]

The Ru–S(thioether) bond lengths, Ru–S(2) and Ru–S(4), are 2.340 (1) and 2.351 (1) Å. These values are approximately 0.04 Å shorter than the comparable values that were observed in $\mathrm{RuBr_2(Me_2SO)((EtS(CH_2)_3)_2SO)}$.[7] The bond lengths between the Ru(II) ion and the sulfoxide S atoms in **9** show a pronounced trans effect.[11] The trans-related Ru–S(sulfoxide) bond lengths, Ru–S(1) and Ru–S(3), for complex **9** are 2.321 (1) and 2.355 (1) Å. These values are very similar to the Ru–S(sulfoxide) bond length (2.360 (1) Å) that was found for *trans*-$\mathrm{RuBr_2(Me_2SO)_4}$.[12] These bond lengths are approximately 0.1 Å longer than the Ru–S(sulfoxide) bond lengths for complexes with halide ligands trans to the sulfoxide donors (2.252 (5) to 2.273 (5) Å in the $\mathrm{RuCl_3(Me_2SO)_3^-}$ ion,[13] 2.277 (1) Å in $\mathrm{RuCl_2(Me_2SO)_4}$,[14] and 2.235 (2) and 2.275 (2) Å in $\mathrm{RuBr_2(Me_2SO)((EtS(CH_2)_3)_2SO)}$[7].

The degree of metal-to-sulfur ($d\pi$–$d\pi$) back-bonding has a pronounced influence on the Ru(II)–S bond lengths and is sensitive to the identity of the ligand that is trans to the S donor. For the complexes containing a Ru(II)–S(sulfoxide) residue that is trans to a good σ-donor and a non-π-acceptor ligand, the Ru–S bond lengths range from 2.188 (3) Å for $\mathrm{Ru(NH_3)_5(Me_2SO)}$[15] to 2.260 (3) Å for $[\mathrm{Ru(Me_2SO\text{-}}S)_3\mathrm{(Me_2SO\text{-}}O)_3](\mathrm{PF_6})_2$.[16] The Ru–S(sulfoxide) bond lengths for complexes such as **9** and *trans*-$\mathrm{RuBr_2(Me_2SO)_4}$,[12] in which the good π-accepting sulfoxide ligands are opposite one another, are considerably longer, and hence these bonds are potentially weaker. Consequently, the trans-related $\mathrm{Me_2SO}$ ligands are expected to exhibit an enhanced lability of the Ru–S(sulfoxide) bonds. Such a labilizing effect arising from a trans geometry could surely be expected to play a role during the catalytic cycle for the all-trans 2,2,2 complexes.

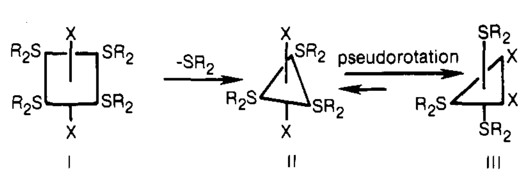
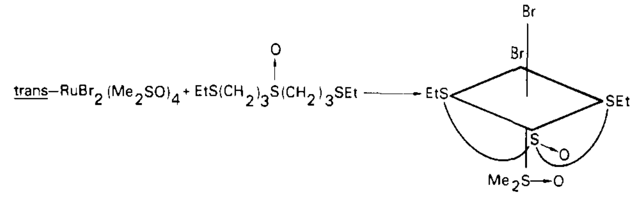


Figure 5. Schematic illustration of the possible dissociative pathways for formation of six-coordinate Ru(II) complexes with linear tridentate ligand **3**.

The unique oxidation potential exhibited by this minor isomer ($E_{1/2}$ = 0.91 V) suggested that it was a 2,2,2 isomer that had not previously been synthesized and characterized. Since only one other structural variation was possible—a trans-sulfoxide, cis, cis complex—it seemed reasonable that this would be the structure of this complex, and indeed it is. Thus, as noted above, each geometry of the 2,2,2 stoichiometry apparently possesses its own unique oxidation potential.

Summary and Conclusions

We have shown herein that all-cis complex **10**, corresponding to isomer C in figure 1 of ref 2, is the major isomer formed in the reaction of ligand **3** with *trans*-$\mathrm{RuBr_2(\overline{S(CH_2)_3CH_2})_4}$[4] and that a minor fraction of least stable isomer E, containing the cis-halo, cis-thioether, cis-sulfoxide geometry, is also obtained. The question arises as to why no amount of isomer D, containing the trans-thioether, cis-halo, cis-sulfoxide geometry is observed in view of our finding in the preceding paper that this is apparently the kinetically accessible and thermodynamically the most stable isomer of the three possible in this series containing the *cis*-dihalo configuration (isomers C, D, and E). As shown there, when $\mathrm{EtS(CH_2)_3SO(CH_2)_3SEt}$ is reacted with *trans*-$\mathrm{RuBr_2(Me_2SO)_4}$, only complex **11** forms. Thus, if ligand **3** folds during chelation and coordinates facially to the Ru(II) ion, we anticipated that this symmetrical structure corresponding to isomer D, with the sulfoxide ends favorably oriented in a trans disposition to the halides (corresponding to complex **11**), would form exclusively. Yet it is isomer C with apparent intermediate thermodynamic stability (only one sulfoxide trans to a halide) that is observed. This dilemma can be resolved by analyzing the course of the substitution reaction by noting that all substitutions would occur via a dissociative pathway involving a five-coordinate Ru(II) intermediate. We assume that chelation occurs before such a five-coordinate intermediate can undergo a subsequent Berry interconversion process[17] and that once the tridentate ligand is bound to the metal at one locus successive binding of the next adjacent donor set of the tridentate ligand occurs directly when an accessible site becomes free on the metal. In Figure 5, the scheme for possible substitution options is shown for this system. As can be seen, there are only four possible initial choices for chelation depending upon whether the tridentate ligand initially



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binds with either a sulfoxide or thioether donor and whether five-coordinate intermediate II or III reacts with ligand **3**.

Inspection of Figure 5 and the scheme in the supplementary material reveals that five-coordinate intermediate II with the *trans*-dihalo configuration cannot give the observed products but would give only the desired all-trans complex. Since this isomer is never observed, this pathway would not be operative. This means that the initial trigonal-bipyramidal intermediate, *trans*-$RuBr_2(S(CH_2)_4)_3$, would undergo an isomerization (pseudorotation) to yield a *cis*-dibromo five-coordinate intermediate (structure III of Figure 5) and finally complexation with ligand 3 would yield the observed products. An analysis of all the possible pathways available for coordination of ligand 3 to five-coordinate intermediate III of Figure 5 is presented in the supplementary material. Nevertheless, observed geometric isomers C (**10**) and E(**9**) are indeed predicted from the complexation pathways that utilize five-coordinate intermediate III (Figure 5).

Thus, it appears that the use of a linear tridentate ligand to generate the all-trans 2,2,2 complex will not succeed. This apparently arises because the *trans*-dihalo geometry of the five-coordinate intermediate is in a very unfavorable equilibrium with the five-coordinate intermediate with the *cis*-dihalo geometry (III of Figure 5). Consequently, the *cis*-dihalo geometry will be more favorable in the products of the substitution reactions, thus limiting their usefulness for the synthesis of the all-trans complexes. In the catalytic situation in which monodentate ligands are present, this problem can apparently be overcome. The subtle electronic factors favoring the cis geometries can be overridden by steric factors that favor the all-trans geometry. When bulkier monodentate substrates are used, the faster rates that are observed[3] are consistent with the formation of a higher concentration of the desired all-trans complex, although very bulky thioether ligands (t-Bu_2S) afford no catalytic activity since complexes of the stoichiometry $RuX_2(R_2S)_2(R_2SO)_2$ do not form in this case.

Acknowledgment is made to L. C. Strickland (of these laboratories) for his assistance with the crystal structure investigation, to R. E. Shumate for his assistance with the syntheses, and to Professor Devon Meek of The Ohio State University for useful discussions.

Registry No. **2**, 101653-80-9; **3**, 101835-53-4; **5**, 101810-60-0; **6**, 101835-55-6; **7**, 101835-54-5; **8**, 101835-56-7; **9**, 101835-57-8; **10**, 101915-10-0.

Supplementary Material Available: Tables of H atom parameters, anisotropic thermal parameters, bond lengths and bond angles, and the numerical description of the pseudomirror plane and a figure illustrating the possible substitution pathways for the reaction between *trans*-$RuBr_2(\overline{S(CH_2)_3CH_2})_4$ and ligand 3 (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (17 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Dynamic, Static, and Theoretical Electron Deformation Density for Binuclear Transition-Metal Complexes: Dicobalt Hexacarbonyl Acetylene

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Received July 31, 1985

The electron deformation density distribution in $Co_2(CO)_6R_2C_2$ ($R = C(CH_3)_3$) has been obtained from low-temperature X-ray and neutron data and from theoretical wave functions at the Hartree–Fock and configuration interaction levels. The experimental determination of the deformation density of $(t\text{-}Bu_2C_2)Co_2(CO)_6$ at 122 K (space group $P\bar{1}$, $a = 8.289$ (2) Å, $b = 8.400$ (2) Å, $c = 13.552$ (2) Å, $\alpha = 88.67$ (2)°, $\beta = 94.45$ (2)°, $\gamma = 106.75$ (4)°, $Z = 2$) does not show accumulation of density along the Co–Co line (Co–Co = 2.462 Å). The static deformation density maps obtained from multipolar refinement display two electron depopulation regions around each Co atom, separated by two peaks. An axis of minimum deformation density can be defined in the vicinity of each cobalt. This axis is collinear with the direction of the bent metal–metal bond defined by quantum-chemical LCAO calculations. The theoretical maps at SCF and CI levels display similar depopulation regions, but four distinct peaks are found around each metal. A "bent-bond peak" is obtained between the acetylene carbon atoms in both the experimental and the theoretical maps. The position of the peak, which is shifted away from the metal–metal line, results from the displacement of the π overlap, in turn caused by the distortion of the acetylenic system. These experimental and theoretical results are compared with the density maps previously published for the isolobal complex $Ni_2(C_5H_5)_2C_2H_2$. Much similarity is obtained between the distributions computed for both complexes and with the experimental maps of the dicobalt system. It seems that the disagreement with the experimental maps of $Ni_2(C_5H_5)_2C_2H_2$ is a consequence of the crystalline acentric and disordered structure of the dinickel complex. Fragment deformation densities have been computed for $Co_2(CO)_6C_2H_2$. The corresponding maps display an important accumulation of density in the π^* orbital of the acetylene carbons, directed toward the Co atoms. The Mulliken population analysis shows that back-donation corresponds to a charge transfer of 0.88 e, balanced by a σ-donation transfer of the same magnitude. A significant peak is also obtained at the center of the metal–metal bent bond. The results illuminate the synergic bonding characteristic of these complexes, where metal–metal interaction, the σ donation, and the π back-donation are involved.

Introduction

The relatively small deformation of the valence part of the electron cloud is known to be the key for bonding energy and molecular structure. The more or less accurate analysis of the electron density distribution in molecules has been for a long time the privilege of theoretical chemistry, which can obtain such a distribution from a computed wave function. Over the last 15 years, however, increasingly accurate X-ray or neutron diffraction experiments have allowed us, according to the term coined by Coppens, to "see the electrons".[2]

Another condition for ensuring the chemical interest of these experimental density distributions is to focus the discussion of the results on this part of the electron cloud, which has been reorganized by chemical bonding. This is obtained by substracting from the observed density distribution of the system another distribution

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